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(54) **PLASMA-BASED CHEMICAL SOURCE
DEVICE AND METHOD OF USE THEREOF**

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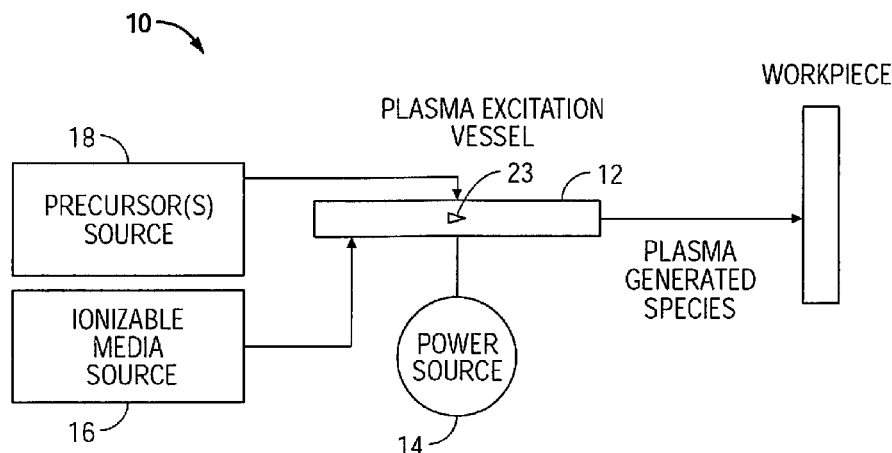
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U.S. PATENT DOCUMENTS

438,257	A	10/1890	Raquet	5,858,477	A	1/1999	Veerasamy et al.
2,213,820	A	9/1940	Maxson	5,865,937	A	2/1999	Shan et al.
2,598,301	A	5/1952	Rajchman	5,866,985	A	2/1999	Coultas et al.
3,134,947	A	5/1964	Charasz	5,869,832	A *	2/1999	Wang et al. 250/288
3,308,050	A *	3/1967	Denis et al. 422/186.03	5,892,328	A	4/1999	Shang et al.
3,434,476	A *	3/1969	Shaw et al. 606/22	5,909,086	A	6/1999	Kim et al.
3,492,074	A *	1/1970	Rendina 356/316	5,945,790	A *	8/1999	Schaefer 315/335
3,687,832	A *	8/1972	Fydelor et al. 204/165	5,955,886	A *	9/1999	Cohen et al. 324/464
3,838,242	A	9/1974	Goucher	5,961,772	A	10/1999	Selwyn
3,903,891	A	9/1975	Brayshaw	5,977,715	A	11/1999	Li et al.
3,938,525	A	2/1976	Coucher	6,013,075	A	1/2000	Avramenko et al.
4,010,400	A	3/1977	Hollister	6,020,794	A	2/2000	Wilbur
4,017,707	A	4/1977	Brown et al.	6,024,733	A	2/2000	Eggers et al.
4,143,337	A	3/1979	Beaulieu	6,027,601	A	2/2000	Hanawa
4,177,422	A	12/1979	Deficis et al.	6,027,617	A *	2/2000	Hayashi et al. 204/170
4,181,897	A	1/1980	Miller	6,030,667	A	2/2000	Nakagawa et al.
4,188,426	A *	2/1980	Auerbach 427/490	6,033,582	A	3/2000	Lee et al.
4,274,919	A	6/1981	Jensen et al.	6,036,878	A	3/2000	Collins
4,337,415	A	6/1982	Dürr	6,046,546	A	4/2000	Porter et al.
4,517,495	A *	5/1985	Piepmeyer 315/111.21	6,047,700	A	4/2000	Eggers et al.
4,577,165	A	3/1986	Uehara et al.	6,053,172	A	4/2000	Hovda et al.
4,629,887	A	12/1986	Bernier	6,063,079	A	5/2000	Hovda et al.
4,629,940	A	12/1986	Gagne et al.	6,063,084	A	5/2000	Farin
4,699,082	A *	10/1987	Hakim 118/716	6,063,937	A	5/2000	Dlubala et al.
4,780,803	A	10/1988	Dede Garcia-Santamaria	6,066,134	A	5/2000	Eggers et al.
4,781,175	A *	11/1988	McGreevy et al. 606/40	6,086,585	A	7/2000	Hovda et al.
4,818,916	A	4/1989	Morrisroe	6,099,523	A	8/2000	Kim et al.
4,837,484	A *	6/1989	Eliasson et al. 313/634	6,102,046	A	8/2000	Weinstein et al.
4,877,999	A	10/1989	Knapp et al.	6,105,581	A	8/2000	Eggers et al.
4,901,719	A	2/1990	Trenconsky et al.	6,109,268	A	8/2000	Thapliyal et al.
4,922,210	A	5/1990	Flachenecker et al.	6,110,395	A	8/2000	Gibson, Jr.
4,956,582	A	9/1990	Bourassa	6,113,597	A	9/2000	Eggers et al.
5,013,959	A *	5/1991	Kogelschatz 313/36	6,132,575	A	10/2000	Pandumsoporn et al.
5,025,373	A	6/1991	Keyser, Jr. et al.	6,137,237	A	10/2000	MacLennan et al.
5,041,110	A *	8/1991	Fleenor 606/34	6,142,992	A	11/2000	Cheng et al.
5,098,430	A	3/1992	Fleenor	6,149,620	A	11/2000	Baker et al.
5,117,088	A *	5/1992	Stava 219/137 PS	6,153,852	A *	11/2000	Blutke et al. 219/121.59
5,124,526	A	6/1992	Muller et al.	6,159,208	A	12/2000	Hovda et al.
5,135,604	A	8/1992	Kumar et al.	6,170,428	B1	1/2001	Redeker et al.
5,155,547	A	10/1992	Casper et al.	6,178,918	B1	1/2001	Van Os et al.
5,159,173	A	10/1992	Frind et al.	6,179,836	B1	1/2001	Eggers et al.
5,180,949	A	1/1993	Durr	6,182,469	B1	2/2001	Campbell et al.
5,194,740	A *	3/1993	Kogelschatz et al. 250/492.1	6,183,655	B1	2/2001	Wang et al.
5,223,457	A	6/1993	Mintz et al.	6,190,381	B1	2/2001	Olsen et al.
5,256,138	A	10/1993	Burek et al.	6,197,026	B1	3/2001	Farin et al.
5,280,154	A	1/1994	Cuomo et al.	6,203,542	B1	3/2001	Ellsberry et al.
5,300,068	A	4/1994	Rosar et al.	6,206,871	B1	3/2001	Zanon et al.
5,304,279	A	4/1994	Coultas et al.	6,206,878	B1 *	3/2001	Bishop et al. 606/49
5,320,621	A	6/1994	Gordon et al.	6,207,924	B1	3/2001	Trassy
5,334,834	A	8/1994	Ito et al.	6,210,402	B1	4/2001	Olsen et al.
RE34,780	E	11/1994	Trenconsky et al.	6,210,410	B1	4/2001	Farin et al.
5,383,019	A	1/1995	Farrell et al.	6,213,999	B1	4/2001	Platt, Jr. et al.
5,384,167	A	1/1995	Nishiwaki et al.	6,222,186	B1	4/2001	Li et al.
5,401,350	A	3/1995	Patrick et al.	6,224,592	B1	5/2001	Eggers et al.
5,449,356	A	9/1995	Walbrink et al.	6,225,593	B1	5/2001	Howieson et al.
5,449,432	A	9/1995	Hanawa	6,228,078	B1	5/2001	Eggers et al.
5,466,424	A *	11/1995	Kusano et al. 422/186.05	6,228,082	B1	5/2001	Baker et al.
5,505,729	A	4/1996	Rau	6,228,229	B1	5/2001	Raaijmakers et al.
5,526,138	A	6/1996	Sato	6,235,020	B1	5/2001	Cheng et al.
5,534,231	A	7/1996	Savas	6,237,526	B1	5/2001	Brcka
5,607,509	A	3/1997	Schumacher et al.	6,238,391	B1	5/2001	Olsen et al.
5,618,382	A	4/1997	Mintz et al.	6,242,735	B1	6/2001	Li et al.
5,683,366	A	11/1997	Eggers et al.	6,248,250	B1	6/2001	Hanawa et al.
5,688,357	A	11/1997	Hanawa	6,252,354	B1	6/2001	Collins et al.
5,697,882	A	12/1997	Eggers et al.	6,254,600	B1	7/2001	Willink et al.
5,708,330	A	1/1998	Rothenbuhler et al.	6,254,738	B1	7/2001	Stimson et al.
5,720,745	A	2/1998	Farin et al.	6,264,650	B1	7/2001	Hovda et al.
5,733,511	A	3/1998	De Francesco	6,264,651	B1	7/2001	Underwood et al.
5,776,255	A *	7/1998	Asaba et al. 118/726	6,264,652	B1	7/2001	Eggers et al.
5,780,862	A *	7/1998	Siess 250/492.3	6,270,687	B1	8/2001	Ye et al.
5,810,764	A	9/1998	Eggers et al.	6,277,112	B1	8/2001	Underwood et al.
5,818,581	A	10/1998	Kurosawa et al.	6,277,251	B1	8/2001	Hwang et al.
5,841,531	A	11/1998	Gliddon	6,283,961	B1	9/2001	Underwood et al.
5,843,019	A	12/1998	Eggers et al.	6,287,980	B1	9/2001	Hanazaki et al.
5,843,079	A	12/1998	Suslov	6,291,938	B1	9/2001	Jewett et al.
5,845,488	A	12/1998	Hancock et al.	6,296,636	B1	10/2001	Cheng et al.
5,849,136	A	12/1998	Mintz et al.	6,296,638	B1	10/2001	Davison et al.
				6,299,948	B1	10/2001	Gherardi et al.
				6,309,387	B1	10/2001	Eggers et al.

6,313,587 B1	11/2001	MacLennan et al.	6,653,594 B2	11/2003	Nakamura et al.
6,326,584 B1	12/2001	Jewett et al.	6,659,106 B1	12/2003	Hovda et al.
6,326,739 B1	12/2001	MacLennan et al.	6,663,017 B2	12/2003	Endres et al.
6,328,760 B1	12/2001	James	6,685,803 B2	2/2004	Lazarovich et al.
6,329,757 B1	12/2001	Morrisroe et al.	6,700,093 B2 *	3/2004	Chiou et al. 219/121.55
6,333,481 B2	12/2001	Augeraud et al.	6,712,811 B2	3/2004	Underwood et al.
6,345,588 B1	2/2002	Stimson	6,719,754 B2	4/2004	Underwood et al.
6,346,108 B1	2/2002	Fischer	6,719,883 B2	4/2004	Stimson
6,348,051 B1	2/2002	Farin et al.	6,723,091 B2	4/2004	Goble et al.
6,353,206 B1	3/2002	Roderick	6,726,684 B1	4/2004	Woloszko et al.
6,355,032 B1	3/2002	Hovda et al.	6,740,842 B2	5/2004	Johnson et al.
6,363,937 B1	4/2002	Hovda et al.	6,746,447 B2	6/2004	Davison et al.
6,365,063 B2	4/2002	Collins et al.	6,763,836 B2	7/2004	Tasto et al.
6,365,864 B1 *	4/2002	Stava 219/50	6,770,071 B2	8/2004	Woloszko et al.
6,375,750 B1	4/2002	Van Os et al.	6,772,012 B2	8/2004	Ricart et al.
6,376,972 B1 *	4/2002	Tarasenko et al. 313/231.01	6,773,431 B2	8/2004	Eggers et al.
6,379,351 B1	4/2002	Thapliyal et al.	6,774,569 B2	8/2004	De Vries et al.
6,387,088 B1	5/2002	Shattuck et al.	6,780,178 B2	8/2004	Palanker et al.
6,391,025 B1	5/2002	Weinstein et al.	6,780,184 B2	8/2004	Tanrisever
6,396,214 B1	5/2002	Grosse et al.	6,781,317 B1	8/2004	Goodman
6,401,652 B1	6/2002	Mohn et al.	6,787,730 B2	9/2004	Coccio et al.
6,407,513 B1 *	6/2002	Vollkommer et al. 315/246	6,805,130 B2	10/2004	Tasto et al.
6,409,933 B1	6/2002	Holland et al.	6,806,438 B2	10/2004	Nakano et al.
RE37,780 E	7/2002	Lanzani et al.	6,815,633 B1	11/2004	Chen et al.
6,416,507 B1	7/2002	Eggers et al.	6,818,140 B2	11/2004	Ding
6,416,508 B1	7/2002	Eggers et al.	6,832,996 B2	12/2004	Woloszko et al.
6,416,633 B1	7/2002	Spence	6,837,884 B2	1/2005	Woloszko
6,419,752 B1 *	7/2002	Shvets et al. 118/720	6,837,887 B2	1/2005	Woloszko et al.
6,424,099 B1	7/2002	Kirkpatrick et al.	6,837,888 B2	1/2005	Ciarrocca et al.
6,424,232 B1	7/2002	Mavretic et al.	6,840,937 B2	1/2005	Van Wyk
6,429,400 B1 *	8/2002	Sawada et al. 219/121.52	6,849,191 B2	2/2005	Ono et al.
6,432,103 B1	8/2002	Ellsberry et al.	6,855,143 B2	2/2005	Davison et al.
6,432,260 B1	8/2002	Mahoney et al.	6,855,225 B1	2/2005	Su et al.
6,443,948 B1	9/2002	Suslov	6,861,377 B1	3/2005	Hirai et al.
6,444,084 B1	9/2002	Collins	6,867,859 B1	3/2005	Powell
6,445,141 B1	9/2002	Kastner et al.	6,876,155 B2	4/2005	Howald et al.
6,459,066 B1	10/2002	Khater et al.	6,890,332 B2	5/2005	Truckai et al.
6,461,350 B1	10/2002	Underwood et al.	6,896,672 B1	5/2005	Eggers et al.
6,461,354 B1	10/2002	Olsen et al.	6,896,674 B1	5/2005	Woloszko et al.
6,464,695 B2	10/2002	Hovda et al.	6,896,775 B2	5/2005	Chistyakov
6,464,889 B1	10/2002	Lee et al.	6,909,237 B1	6/2005	Park et al.
6,464,891 B1	10/2002	Druz et al.	6,915,806 B2	7/2005	Pacek et al.
6,468,270 B1	10/2002	Hovda et al.	6,919,527 B2	7/2005	Boulos et al.
6,468,274 B1	10/2002	Alleyne et al.	6,920,883 B2	7/2005	Bessette et al.
6,471,822 B1	10/2002	Yin et al.	6,921,398 B2	7/2005	Carmel et al.
6,474,258 B2	11/2002	Brcka	6,922,093 B2	7/2005	Kanda
6,475,215 B1 *	11/2002	Tanrisever 606/45	6,924,455 B1	8/2005	Chen et al.
6,482,201 B1	11/2002	Olsen et al.	6,929,640 B1	8/2005	Underwood et al.
6,488,825 B1 *	12/2002	Hilliard 204/298.06	6,949,096 B2	9/2005	Davison et al.
6,497,826 B2	12/2002	Li et al.	6,949,887 B2	9/2005	Kirkpatrick et al.
6,500,173 B2	12/2002	Underwood et al.	6,958,063 B1	10/2005	Soil et al.
6,501,079 B1 *	12/2002	Furuya 250/437	6,974,453 B2	12/2005	Woloszko et al.
6,502,416 B2	1/2003	Kawasumi et al.	6,991,631 B2	1/2006	Woloszko et al.
6,502,588 B2	1/2003	Li et al.	7,004,941 B2	2/2006	Tvinnereim et al.
6,504,307 B1 *	1/2003	Malik et al. 315/111.21	7,019,253 B2	3/2006	Johnson et al.
6,507,155 B1	1/2003	Barnes et al.	7,046,088 B2	5/2006	Ziegler
6,525,481 B1	2/2003	Klima et al.	7,048,733 B2	5/2006	Hartley et al.
6,534,133 B1 *	3/2003	Kaloyeros et al. 427/576	7,070,596 B1	7/2006	Woloszko et al.
6,540,741 B1	4/2003	Underwood et al.	7,084,832 B2	8/2006	Pribyl
6,544,261 B2	4/2003	Ellsberry et al.	7,090,672 B2	8/2006	Underwood et al.
6,565,558 B1	5/2003	Lindenmeier et al.	7,096,819 B2	8/2006	Chen et al.
6,575,968 B1	6/2003	Eggers et al.	7,100,532 B2	9/2006	Pribyl
6,579,289 B2	6/2003	Schnitzler	7,104,986 B2	9/2006	Hovda et al.
6,579,426 B1	6/2003	Van Gogh et al.	7,115,185 B1	10/2006	Gonzalez et al.
6,582,423 B1	6/2003	Thapliyal et al.	7,122,035 B2	10/2006	Canady
6,582,427 B1	6/2003	Goble et al.	7,122,965 B2	10/2006	Goodman
6,582,429 B2	6/2003	Krishnan et al.	7,131,969 B1	11/2006	Hovda et al.
6,589,237 B2	7/2003	Woloszko et al.	7,132,620 B2	11/2006	Coelho et al.
6,589,437 B1	7/2003	Collins	7,132,996 B2	11/2006	Evans et al.
6,595,990 B1	7/2003	Weinstein et al.	7,150,745 B2	12/2006	Stern et al.
6,617,794 B2	9/2003	Barnes et al.	7,157,857 B2	1/2007	Brouk et al.
6,624,583 B1	9/2003	Coll et al.	7,160,521 B2	1/2007	Porshnev et al.
6,625,555 B2	9/2003	Kuan et al.	7,161,112 B2	1/2007	Smith et al.
6,629,974 B2	10/2003	Penny et al.	7,164,484 B2	1/2007	Takahashi et al.
6,632,193 B1	10/2003	Davison et al.	7,166,816 B1	1/2007	Chen et al.
6,632,220 B1	10/2003	Eggers et al.	7,179,255 B2	2/2007	Lettice et al.
6,642,526 B2	11/2003	Hartley	7,186,234 B2	3/2007	Dahla et al.
6,646,386 B1	11/2003	Sirkis et al.	7,189,939 B2	3/2007	Lee et al.
6,652,717 B1	11/2003	Hong	7,189,940 B2	3/2007	Kumar et al.

7,192,428 B2	3/2007	Eggers et al.	2002/0092826 A1	7/2002	Ding
7,199,399 B2	4/2007	Chin-Lung et al.	2002/0125207 A1	9/2002	Ono et al.
7,201,750 B1	4/2007	Eggers et al.	2002/0132380 A1	9/2002	Nakano et al.
7,214,280 B2	5/2007	Kumar et al.	2003/0006019 A1	1/2003	Johnson et al.
7,214,934 B2	5/2007	Stevenson	2003/0036753 A1	2/2003	Morgan et al.
7,217,268 B2	5/2007	Eggers et al.	2003/0038912 A1 *	2/2003	Broer et al. 349/122
7,217,903 B2	5/2007	Bayer et al.	2003/0047540 A1 *	3/2003	Konavko et al. 219/121.4
7,220,261 B2	5/2007	Truckai et al.	2003/0069576 A1 *	4/2003	Tanrisever 606/41
7,227,097 B2	6/2007	Kumar et al.	2003/0075522 A1	4/2003	Weichart et al.
7,238,185 B2	7/2007	Palanker et al.	2003/0132198 A1	7/2003	Ono et al.
7,241,293 B2	7/2007	Davison	2003/0158545 A1	8/2003	Hovda et al.
7,270,658 B2	9/2007	Woloszko et al.	2004/0007985 A1	1/2004	De Vries et al.
7,270,659 B2	9/2007	Ricart et al.	2004/0022669 A1	2/2004	Ruan et al.
7,270,661 B2	9/2007	Dahla et al.	2004/0075375 A1	4/2004	Miyashita et al.
7,271,363 B2	9/2007	Lee et al.	2004/0086434 A1	5/2004	Gadgil et al.
7,275,344 B2	10/2007	Woodmansee, III et al.	2004/0129212 A1	7/2004	Gadgil et al.
7,276,063 B2	10/2007	Davison et al.	2004/0140194 A1	7/2004	Taylor et al.
7,282,244 B2	10/2007	Schaeppkens et al.	2004/0186470 A1 *	9/2004	Goble et al. 606/41
7,291,804 B2	11/2007	Suslov	2005/0017646 A1	1/2005	Boulos et al.
7,292,191 B2	11/2007	Anderson	2005/0103748 A1	5/2005	Yamaguchi et al.
7,297,143 B2	11/2007	Woloszko et al.	2005/0118350 A1	6/2005	Koulik et al.
7,297,145 B2	11/2007	Woloszko et al.	2005/0149012 A1	7/2005	Penny et al.
7,298,091 B2	11/2007	Pickard et al.	2005/0153159 A1 *	7/2005	Sugiyama et al. 428/632
7,309,843 B2	12/2007	Kumar et al.	2005/0205212 A1	9/2005	Singh et al.
7,316,682 B2	1/2008	Konesky	2005/0236374 A1 *	10/2005	Blankenship 219/121.11
7,318,823 B2	1/2008	Sharps et al.	2006/0009763 A1 *	1/2006	Goble et al. 606/49
7,331,957 B2	2/2008	Woloszko et al.	2006/0011465 A1	1/2006	Burke et al.
7,353,771 B2	4/2008	Millner et al.	2006/0017388 A1	1/2006	Stevenson
7,355,379 B2	4/2008	Kitamura et al.	2006/0038992 A1	2/2006	Morrisroe
7,357,798 B2	4/2008	Sharps et al.	2006/0065628 A1	3/2006	Vahedi et al.
7,361,175 B2	4/2008	Suslov	2006/0091109 A1 *	5/2006	Partlo et al. 216/63
7,387,625 B2	6/2008	Hovda et al.	2006/0175015 A1	8/2006	Chen et al.
7,393,351 B2	7/2008	Woloszko et al.	2006/0266735 A1	11/2006	Shannon et al.
7,399,944 B2	7/2008	DeVries et al.	2006/0278254 A1	12/2006	Jackson
7,410,669 B2	8/2008	Dieckhoff et al.	2007/0021747 A1	1/2007	Suslov
7,419,488 B2	9/2008	Ciarrocca et al.	2007/0021748 A1 *	1/2007	Suslov 606/45
7,426,900 B2	9/2008	Brcka	2007/0027440 A1 *	2/2007	Altshuler et al. 606/9
7,429,260 B2	9/2008	Underwood et al.	2007/0029292 A1	2/2007	Suslov
7,429,262 B2	9/2008	Woloszko et al.	2007/0029500 A1 *	2/2007	Coulombe et al. 250/423 F
7,431,857 B2	10/2008	Shannon et al.	2007/0045561 A1 *	3/2007	Cooper 250/453.11
7,435,247 B2	10/2008	Woloszko et al.	2007/0068899 A1 *	3/2007	Yoon 156/345.43
7,442,191 B2	10/2008	Hovda et al.	2007/0072433 A1 *	3/2007	Yoon et al. 438/707
7,449,021 B2	11/2008	Underwood et al.	2007/0075652 A1 *	4/2007	Espiau et al. 315/248
7,453,403 B2	11/2008	Anderson	2007/0084563 A1	4/2007	Holland
7,459,899 B2	12/2008	Mattaboni et al.	2007/0087455 A1	4/2007	Hoffman
7,468,059 B2	12/2008	Eggers et al.	2007/0154363 A1 *	7/2007	Joshi et al. 422/186.04
7,480,299 B2	1/2009	O'Keeffe et al.	2007/0210035 A1	9/2007	Twarog et al.
7,489,206 B2	2/2009	Kotani et al.	2007/0251920 A1	11/2007	Hoffman
7,491,200 B2	2/2009	Underwood	2007/0258329 A1	11/2007	Winey
7,498,000 B2	3/2009	Pekshev et al.	2008/0023443 A1	1/2008	Paterson et al.
7,506,014 B2	3/2009	Drummond	2008/0050291 A1	2/2008	Nagasawa
7,507,236 B2	3/2009	Eggers et al.	2008/0083701 A1	4/2008	Shao et al.
7,510,665 B2	3/2009	Shannon et al.	2008/0099434 A1	5/2008	Chandrachood et al.
7,511,246 B2	3/2009	Morris roe	2008/0099435 A1	5/2008	Grimbergen
7,563,261 B2	7/2009	Carmel et al.	2008/0099436 A1	5/2008	Grimbergen
7,566,333 B2	7/2009	Van Wyk et al.	2008/0122252 A1	5/2008	Corke et al.
7,589,473 B2	9/2009	Suslov	2008/0179290 A1	7/2008	Collins et al.
7,611,509 B2	11/2009	Van Wyk	2008/0185366 A1	8/2008	Suslov
7,632,267 B2	12/2009	Dahla	2008/0268172 A1	10/2008	Fukuda et al.
7,633,231 B2	12/2009	Watson	2008/0284506 A1	11/2008	Messer
7,666,478 B2	2/2010	Paulussen et al.	2008/0292497 A1	11/2008	Vangeneugden et al.
7,691,101 B2	4/2010	Davison et al.	2009/0039789 A1	2/2009	Nikolay
7,708,733 B2	5/2010	Sanders et al.	2009/0039790 A1 *	2/2009	Suslov 315/111.21
7,715,889 B2	5/2010	Ito	2009/0054896 A1	2/2009	Fridman et al.
7,758,575 B2	7/2010	Beller	2009/0064933 A1	3/2009	Liu et al.
7,824,398 B2	11/2010	Woloszko et al.	2010/0089742 A1	4/2010	Suslov
7,879,034 B2	2/2011	Woloszko et al.	2010/0130973 A1	5/2010	Choi et al.
7,887,891 B2	2/2011	Rius	2011/0101862 A1 *	5/2011	Koo et al. 315/111.21
7,892,223 B2	2/2011	Geiselhart	2013/0059273 A1 *	3/2013	Koo et al. 433/216
7,892,230 B2	2/2011	Woloszko	2013/0062014 A1 *	3/2013	Koo et al. 156/345.11
7,901,403 B2	3/2011	Woloszko et al.	2013/0116682 A1 *	5/2013	Koo et al. 606/41
7,940,008 B2	5/2011	Mattaboni et al.	2013/0261536 A1 *	10/2013	Sartor 604/23
7,949,407 B2	5/2011	Kaplan et al.	2014/0224643 A1 *	8/2014	Collins et al. 204/164
8,994,270 B2 *	3/2015	Koo et al. 315/111.21	2014/0225495 A1 *	8/2014	Koo et al. 313/13
9,028,656 B2 *	5/2015	Koo et al. 204/164	2014/0225498 A1 *	8/2014	Koo et al. 313/231.31
2001/0054601 A1	12/2001	Ding			
2002/0014832 A1	2/2002	Moradi et al.			
2002/0022836 A1 *	2/2002	Goble et al. 606/34			
2002/0023899 A1	2/2002	Khater et al.			

FOREIGN PATENT DOCUMENTS

DE	3710489	11/1987	
DE	4139029	6/1993	
DE	4326037	2/1995	
DE	9117019	4/1995	
DE	19537897	3/1997	
DE	9117299	4/2000	
DE	19848784	5/2000	
DE	29724247	8/2000	
DE	19524645	11/2002	
EP	0016542	B1	10/1980
EP	0 495 699	B1	7/1992
EP	0602764	A1	6/1994
EP	0956827		11/1999
EP	1174901	A2	1/2002
FR	1340509		9/1963
JP	61-159953		7/1986
JP	62-130777		6/1987
JP	03-149797		6/1991
JP	H06-119995	A	4/1994
JP	8-243755		9/1996
JP	2000-286094	A	10/2000
JP	2000286094	A	10/2000
JP	2001-501485	A	2/2001
JP	2001332399	A	11/2001
JP	2003007497	A	1/2003
JP	2003049276	A	2/2003
JP	2003093869	A	4/2003
JP	2005-522824	A	7/2005
JP	2005-526904	A	9/2005
JP	2005-528737	A	9/2005
JP	2005276618	A	10/2005
JP	2006114450	A	4/2006
JP	2006310101	A	11/2006
JP	2007188748	A	7/2007
JP	2007207540	A	8/2007
JP	2008041495	A	2/2008
JP	2008071656	A	3/2008
JP	2010-242857		10/2010
SU	1438745		11/1988
WO	WO 99/01887		1/1999
WO	WO 99/36940		7/1999
WO	WO 01/39555	A1	5/2001
WO	03/085693	A1	10/2003
WO	2004032176	A1	4/2004
WO	2004094306	A1	11/2004
WO	WO 2006/116252	A2	11/2006
WO	WO 2006116828	A1 *	11/2006 A61L 2/10
WO	WO 2009036579	A1 *	3/2009 H01J 37/32
WO	2009/146432	A1	12/2009
WO	2010008062	A1	1/2010

OTHER PUBLICATIONS

Jan-Otto Carlsson "Chemical Vapor Deposition," Chapter 7 in R.F. Bunshah, Ed., "Handbook of Deposition Technologies for Films and Coatings (2nd Edition)," William Andrew Publishing/Noyes (1994) pp. 400, 411-413 & 457.*

"Fundamentals of Mass Flow Control," Advanced Energy Industries, Inc., Fort Collins, Co. US (2005) pp. 1-5.*

M.I. Lomaev et al., "Capacitive and Barrier Discharge Excilamps and Their Applications (Review)," Instruments and Experimental Techniques, vol. 49, No. 5, (2006) pp. 595-616.*

E. A. Sosnin et al., "Applications of Capacitive and Barrier Discharge Excilamps in Photoscience," Journal of Photochemistry and Photobiology C: Photochemistry Reviews 7 (2006) pp. 145-163.*

V. F. Tarasenko et al., "VUV and UV Excilamps and Their Applications," High Power Laser Ablation VI, edited by C. R. Phipps, Proc. of Society of Photo-Optical Instrumentation Engineers (SPIE) vol. 6261 (2006) 626136.*

T. Oppenlaender et al., "Mercury-free Vacuum-(VUV) and UV Excilamps: Lamps of the Future?" International Ultraviolet Association (IUVA) News, vol. 7, No. 4 (20058) pp. 16-20.*

M.I. Lomaev et al., "Excilamps and Their Applications (Review)," Progress in Quantum Electronics 36 (2012) 51-97.*

National Instruments Corporation. "LabVIEW(TM): Getting Started with LabVIEW." Apr. 2003 Edition, Part No. 323427-01. pp. i thru i-5 (78 pages). Source location: <http://www.ni.com/manuals/>. Available: <http://www.ni.com/pdf/manuals/323427a.pdf>. Accessed: Feb. 27, 2015.*

Valérie Léveillé. "A Miniature Atmospheric Pressure Glow Discharge Torch for Localized Biomedical Applications," Doctoral Thesis, McGill University, Montréal, Canada. 2006. pp. 1-146. Available: http://digitool.Library.McGill.CA:80/R/-?func=dbin-jump-full&object_id=102676&silolibrary=GEN01. Accessed: Feb. 25, 2015.*

Sara Yonson. "Cell Treatment and Surface Functionalization Using the Atmospheric Pressure Glow Discharge Plasma Torch (APGD-t)," Masters Thesis, McGill University, Montréal, Canada. 2006. pp. 1-77. Available: http://digitool.Library.McGill.CA:80/R/-?func=dbin-jump-full&object_id=99551&silolibrary=GEN01. Accessed: Feb. 26, 2015.*

U.S. Appl. No. 09/270,856, filed Mar. 17, 1999, Gene H. Arts.

U.S. Appl. No. 12/791,100, filed Jun. 1, 2010, Kristin D. Johnson.

U.S. Appl. No. 12/845,842, filed Jul. 29, 2010, Kristin D. Johnson. Hernandez et al., "A Controlled Study of the Argon Beam Coagulator for Partial Nephrectomy," The Journal of Urology, vol. 143, (May 1990) J. Urol. 143: pp. 1062-1065.

Ward et al., "A Significant New Contribution to Radical Head and Neck Surgery," Arch Otolaryngology, Head and Neck Surg., vol. 115 pp. 921-923 (Aug. 1989).

Lieberman et al., "Capacitive Discharges", Principles of Plasma Discharges and Materials Processing, John Wiley & Son, Inc. (2005) pp. 387-460.

Moore et al., "Confined Geometry Interactions of Downstream RF-Excited Atmospheric Plasma Wires", IEEE Transactions on Plasma Science, 0093-3813, (2008) pp. 1-2.

Walsh et al., "Contrasting Characteristics of Pulsed and Sinusoidal Cold Atmospheric Plasma Jets", Applied Physics Letters, 88, 171501 (2006) pp. 1-3.

Cho et al., "Coplanar ac Discharges Between Cylindrical Electrodes With a Nanoporous Alumina Dielectric: Modular Dielectric Barrier Plasma Devices", IEEE Transactions on Plasma Science, vol. 33, No. 2, (Apr. 2005) pp. 378-379.

Xu et al., "DBD Plasma Jet in Atmospheric Pressure Argon", IEEE Transactions on Plasma Science, vol. 36, No. 4, (Aug. 2008), pp. 1352-1353.

Alfred Grill, "Electron Cyclotron Resonance Plasmas", Cold Plasma in Materials Fabrication, IEEE Press (1994) pp. 40-43.

Brand et al., "Electrosurgical Debulking of Ovarian Cancer: A New Technique Using the Argon Beam Coagulator", Gynecologic Oncology 39 pp. 115-118 (1990).

Grund et al., "Endoscopic Argon Plasma . . . Flexible Endoscopy", Endoscopic Surgery and Allied Technologies, No. 1, vol. 2, pp. 42-46 (Feb. 1994).

Waye et al., "Endoscopic Treatment Options", Techniques in Therapeutic Endoscopy, pp. 1.7-1.15, (1987).

B.D. Cullity, "Introduction to Magnetic Materials", University of Notre Dame; Addison-Wesley Publishing Company, Reading MA., (1972) pp. 23-28.

Brian Chapman, "Matching Networks", Glow Discharge Processes, John Wiley & Sons Inc., NY, (1980) pp. 153-172.

Yin et al., "Miniaturization of Inductively Coupled Plasma Sources", IEEE Transactions on Plasma Science, vol. 27, No. 5, (Oct. 1999) pp. 1516-1524.

Park et al., "Nanoporous Anodic Alumina Film on Glass: Improving Transparency by an Ion-Drift Process", Electrochemical and Solid-State Letters, 8 (3) (2005), pp. D5-D7.

P.A. Tulle, "Off-Resonance Microwave-Created Plasmas", Plasma Physics, Pergamon Press (1973) vol. 15, pp. 971-976.

Lieberman et al., "Ohmic Heating", Principles of Plasma Discharges and Materials Processing, John Wiley & Son, Inc. (2005) pp. 97-98.

Lieberman et al., "Optical Actinometry", Principles of Plasma Discharges and Materials Processing, John Wiley & Son, Inc. (2005) pp. 277-279.

Cho et al., "Ozone Production by Nanoporous Dielectric Barrier Glow Discharge in Atmospheric Pressure Air", Applied Physics Letters, 92, 101504, (2008) pp. 1-3.

- Lieberman et al., "Particle and Energy Balance in Discharges", Principles of Plasma Discharges and Materials Processing, John Wiley & Son, Inc. (2005) pp. 329-381.
- Woloszko et al., "Plasma Characteristics of Repetitively-Pulsed Electrical Discharges in Saline Solutions Used for Surgical Procedures", IEEE Transactions of Plasma Science, vol. 30, No. 3, (Jun. 2002) pp. 1376-1383.
- Stoffels et al., "Plasma Needle for In Vivo Medical Treatment: Recent Developments and Perspectives", Plasma Sources Science and Technology 15 (2006) pp. 169-180.
- Schaper et al., "Plasma Production and Vapour Layer Production at a Pulse Power Electrode in Saline Solution:", (2008) www.escampig2008.csic.es/PosterSessions/100.
- Akitsu et al., "Plasma Sterilization Using Glow Discharge at Atmospheric Pressure", Surface & Coatings Technology 193, (2005) pp. 29-34.
- Koo et al., "Room-temperature Slot Microplasma in Atmospheric Pressure Air Between Cylindrical Electrodes With a Nanoporous Alumina Dielectric", Applied Physics Letters, 91, 041502 (2007) pp. 1-3.
- Brian Chapman, "Secondary Electron Emission", Glow Discharge Processes, John Wiley & Sons Inc., NY, (1980) pp. 82-138.
- Moore et al., "Sensitive, Noninvasive, In-Situ Measurement of Temporally and Spatially Resolved Plasma Electric Fields", Physical Review Letters, vol. 52, No. 7, (Feb. 13, 1984) pp. 538-541.
- Lieberman et al., "Sheaths", Principles of Plasma Discharges and Materials Processing, John Wiley & Son, Inc. (2005) pp. 11-14.
- Farin et al., Technology of Argon Plasma . . . Endoscopic Applications; Endoscopic Surgery and Allied Technologies, No. 1, vol. 2, pp. 71-77 (Feb. 1994).
- Lieberman et al., "The Collisionless Sheath", Principles of Plasma Discharges and Materials Processing, John Wiley & Son, Inc. (2005) pp. 167-206.
- Gupta et al., "The Potential of Pulsed Underwater Streamer Discharges as a Disinfection Technique", IEEE Transactions on Plasma Science, vol. 36, No. 4, (Aug. 2008) pp. 1621-1632.
- Mark H. Mellow, "The Role of Endoscopic Laser Therapy in Gastrointestinal Neoplasms", Advanced Therapeutic Endoscopy, pp. 17-21, (1990).
- Silverstein et al., "Thermal Coagulation Therapy for Upper Gastrointestinal Bleeding", Advanced Therapeutic Endoscopy, pp. 79-84, 1990.
- European Search Report EP 01 10 2843.8, dated May 15, 2001.
- European Search Report EP 05 00 2257, dated Jun. 1, 2005.
- European Search Report EP 05 01 8087, dated Oct. 17, 2005.
- European Search Report EP 06 01 9572 dated Nov. 21, 2006.
- European Search Report EP 07 00 4356 dated Jul. 2, 2007.
- European Search Report EP 07 00 4659 dated Feb. 19, 2008.
- European Search Report EP 07 00 4659—partial dated May 24, 2007.
- European Search Report EP 09 00 4975 dated Sep. 11, 2009.
- European Search Report EP 09 01 0519 dated Nov. 16, 2009.
- European Search Report EP 09 01 0520 dated Dec. 10, 2009.
- European Search Report EP 09 01 5212.5 dated Apr. 1, 2010.
- European Search Report EP 09 17 1599.5 dated Mar. 16, 2010.
- European Search Report EP 09 17 1600.1 dated Jan. 26, 2010.
- European Search Report EP 10 174107.2 dated Nov. 5, 2010.
- European Search Report EP 10 180 912.7 dated Dec. 8, 2010.
- European Search Report EP 10 186524.4 dated Feb. 18, 2011.
- International Search Report PCT/US98/19284, dated Jan. 14, 1999.
- Supplementary European Search Report from Appl. No. EP 09 75 5799 mailed Aug. 31, 2012.
- Extended European Search Report issued in Appl. No. 10849146.5 dated Sep. 9, 2013.
- Extended European Search Report corresponding to European Application No. 09755793.8, dated Jul. 21, 2014; 8 pages.
- European Search Report corresponding to European Application No. 09 84 5328, dated Dec. 11, 2014; 8 pages.
- European Search Report dated Dec. 9, 2014, corresponding to European Application No. 09 84 5329; 8 pages.
- Y. Ushio, et al., "General Film Behaviour 299 Secondary Electron Emission Studies on MgO Films," Thin Solid Films, Jan. 1, 1988; pp. 299-308.
- Japanese Notice of Final Rejection and Denial of Entry of Amendment (with English translation), issued Apr. 2, 2015, corresponding to Japanese Patent Application No. 2012-513022; 10 total pages.
- European Communication/Examination Report dated Jul. 14, 2015, corresponding to European Patent Application No. 09 845 329.3; 8 pages.
- European Communication dated Oct. 22, 2015, corresponding to European Application No. 09 755 793.8; 9 pages.
- Japanese Office Action (with English translation), dated Nov. 17, 2015, corresponding to Japanese Application No. 2015-009663; 8 total pages.
- Extended European Search Report corresponding to European Application No. 09755793.8, dated Jul. 21, 2014; 8 pages.
- Japanese Notice of Final Rejection and Denial of Entry of Amendment (with English translation), dated Jun. 2, 2015, corresponding to Japanese Patent Application No. 2013-502548; 15 total pages.
- English translation of Japanese Notice of Reasons for Rejection, dated Feb. 18, 2014, corresponding to Japanese Patent Application No. 2013-502548; 6 pages.
- English translation of Japanese Notice of Reasons for Rejection, dated Oct. 7, 2014, corresponding to Japanese Patent Application No. 2013-502548; 5 pages.
- Australian Patent Examination Report No. 1, dated Apr. 17, 2014, corresponding to Australian Patent Application No. 2010349784; 3 pages.
- European Communication dated Jun. 17, 2014, corresponding to European Patent Application No. 10849146.5; 6 pages.
- International Search Report, dated Nov. 20, 2009, corresponding to International Patent Application No. PCT/US09/05385; 2 pages.
- Mark A. Sobolewski, "Current and Voltage Measurements in the Gaseous Electronics Conference RF Reference Cell," Journal of Research of the National Institute of Standards and Technology, vol. 100, No. 4, Jul.-Aug. 1995; pp. 341-351.
- International Search Report, dated Dec. 4, 2009, corresponding to International Patent Application No. PCT/US09/05389; 2 pages.
- International Search Report, dated Apr. 5, 2010, corresponding to International Patent Application No. PCT/US09/05398; 2 pages.
- International Search Report, dated Nov. 25, 2009, corresponding to International Patent Application No. PCT/US09/05389; 2 pages.

* cited by examiner

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(57)

ABSTRACT

The present disclosure provides for a plasma system including a plasma device coupled to a power source, an ionizable media source and a precursor source. During operation, the ionizable media source provides ionizable media and the precursor ionizable media source provides one or more chemical species, photons at specific wavelengths, as well as containing various reactive functional groups and/or components to treat the workpiece surface by working in concert for synergetic selective tissue effects. The chemical species and the ionizable gas are mixed either upstream or midstream from an ignition point of the plasma device and once mixed, are ignited therein under application of electrical energy from the power source. As a result, a plasma effluent and photon source is formed, which carries the ignited plasma feedstock and resulting mixture of reactive species to a workpiece surface to perform a predetermined reaction.

14 Claims, 6 Drawing Sheets

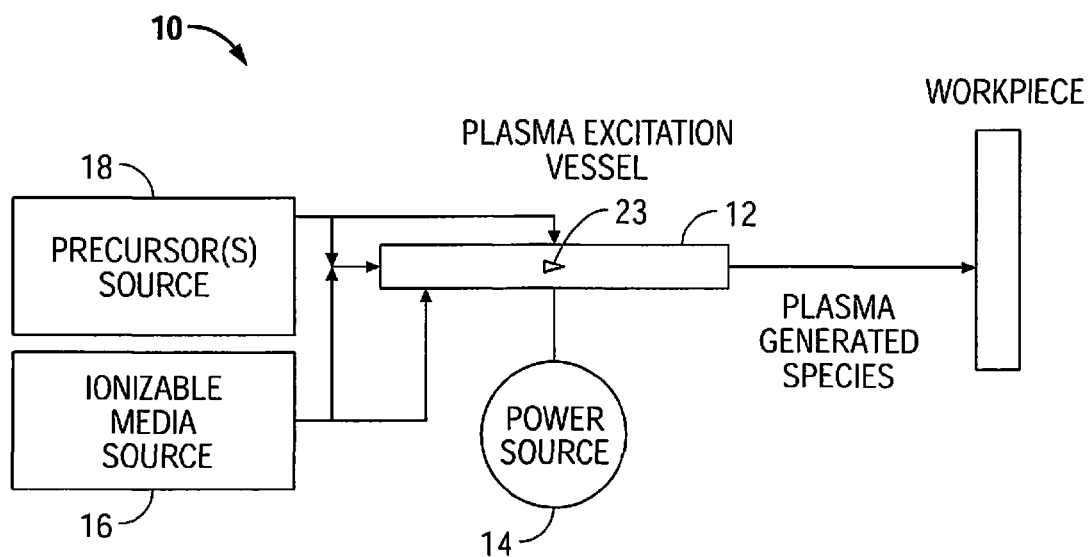


FIG. 1A

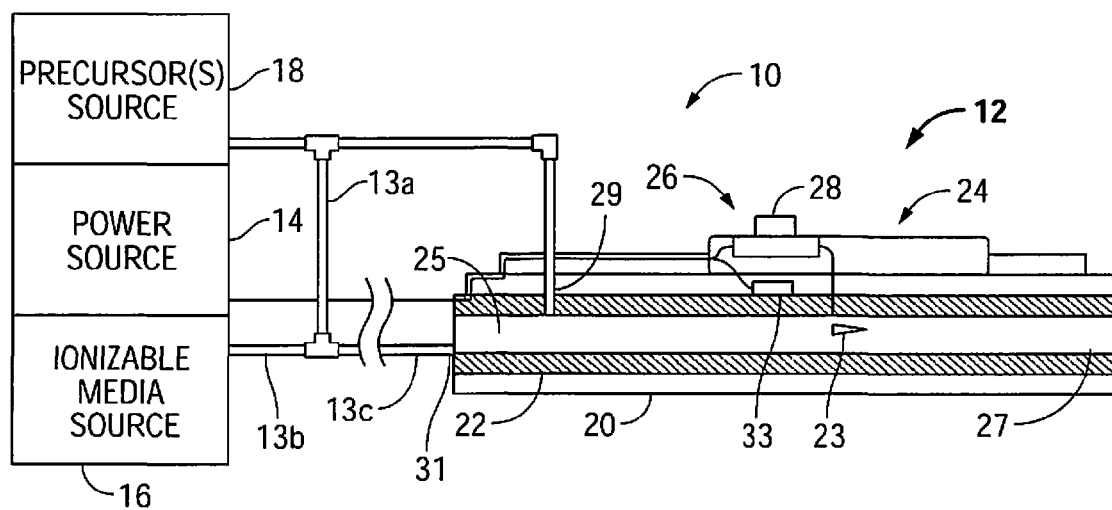


FIG. 2

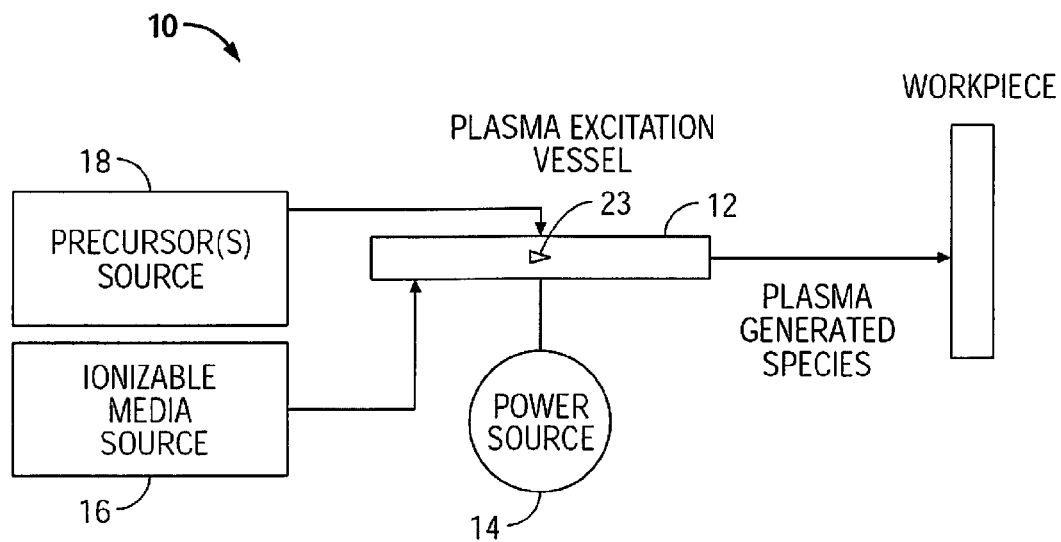


FIG. 1B

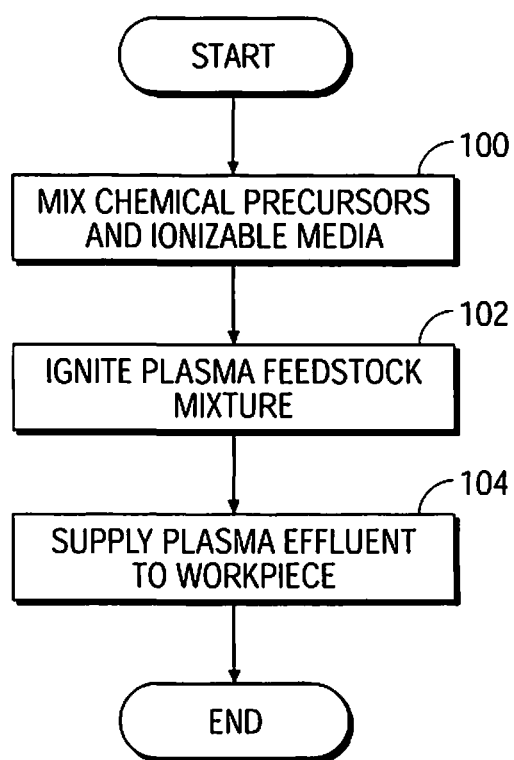
**FIG. 3**

FIG. 4

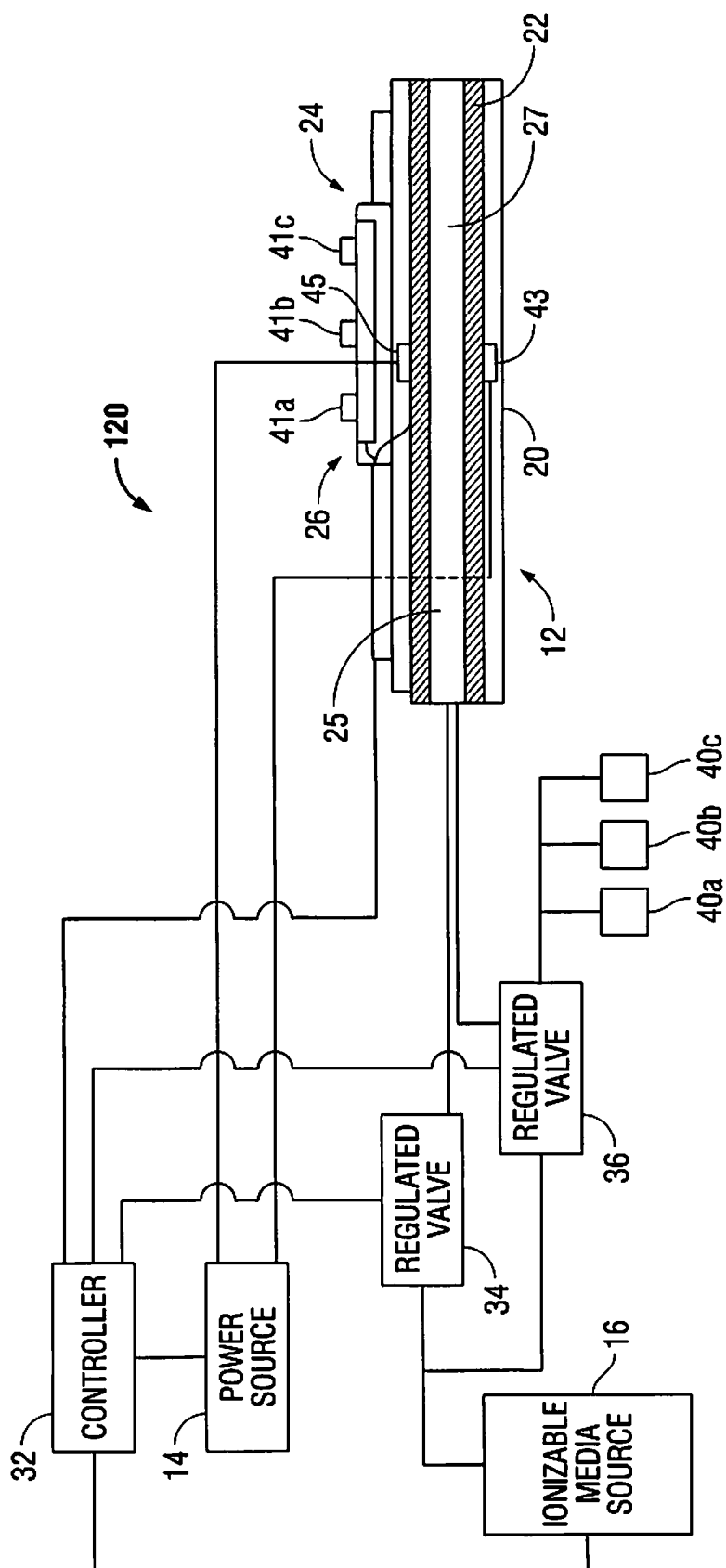


FIG. 5

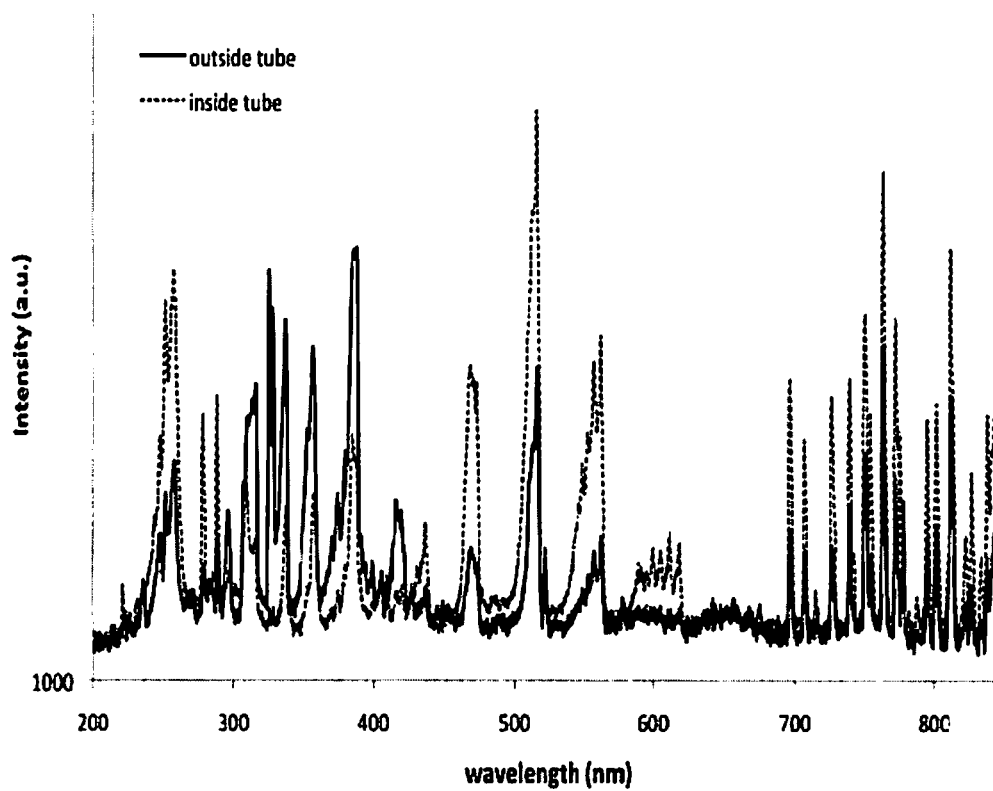


FIG. 6

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PLASMA-BASED CHEMICAL SOURCE DEVICE AND METHOD OF USE THEREOF

CROSS-REFERENCE TO RELATED APPLICATION

The present application claims the benefit of and priority to U.S. Provisional Application Ser. No. 61/057,667 entitled "PLASMA-BASED CHEMICAL SOURCE DEVICE AND METHOD OF USE THEREOF" filed by Moore et al. on May 30, 2008, the entire contents of which are incorporated by reference herein.

BACKGROUND

1. Technical Field

The present disclosure relates to plasma devices and processes for surface processing and material removal or deposition. More particularly, the disclosure relates to an apparatus and method for generating and directing chemically reactive plasma-generated species in a plasma device along with excited-state species (e.g., energetic photons) that are specific to the selected ingredients.

2. Background of Related Art

Electrical discharges in dense media, such as liquids and gases at or near atmospheric pressure, can, under appropriate conditions, result in plasma formation. Plasmas have the unique ability to create large amounts of chemical species, such as ions, radicals, electrons, excited-state (e.g., metastable) species, molecular fragments, photons, and the like. The plasma species may be generated in a variety of internal energy states or external kinetic energy distributions by tailoring plasma electron temperature and electron density. In addition, adjusting spatial, temporal and temperature properties of the plasma allows for achieving specific changes to the material being irradiated by the plasma species and associated photon fluxes. Plasmas are also capable of generating photons including energetic ultraviolet photons that have sufficient energy to initiate photochemical and photocatalytic reaction paths in biological and other materials that are irradiated by the plasma photons.

SUMMARY

Plasma has broad applicability to provide alternative solutions to industrial, scientific and medical needs, especially workpiece surface processing at low temperature. Plasmas may be delivered to a workpiece, thereby affecting many changes in the properties of materials upon which they impinge. One suitable application of the unique chemical species that are produced is to drive non-equilibrium or selective chemical reactions at the workpiece. Such selective processes are especially sought in biological tissue processing, which allows for cutting and removal of tissue at low temperatures with differential selectivity to underlayers and adjacent tissues. That is, the plasma may remove a distinct upper layer of a workpiece but have little or no effect on a separate underlayer of the workpiece or it may be used to selectively remove a particular tissue from a mixed tissue region or selectively remove a tissue with minimal effect to adjacent organs of different tissue type. More specifically, the plasma species are capable of modifying the chemical nature of tissue surfaces by breaking chemical bonds, substituting or replacing surface-terminating species (e.g., surface functionalization) through volatilization, gasification or dissolution of surface materials (e.g., etching). By proper choices of conditions one can remove a tissue type entirely but not effect a nearby

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different tissue type at all when selectivity of the plasma chemistry is tailored to be high.

In one aspect, the present disclosure provides for a plasma system including a plasma device coupled to a power source, an ionizable media source and a precursor source. During operation, the ionizable media source provides ionizable media suitable for plasma initiation and maintenance and the precursor source provides one or more chemical species having various reactive functional groups and/or components that are desired for surface treatment. The chemical species and the ionizable media are mixed upstream or at ignition point of the plasma device and, once mixed, are ignited under application of electrical energy from the power source. The ignited media forms a volume of active plasma in the region where electrical energy is delivered. The active plasma volume includes various species that flow therefrom as an effluent that is delivered to a workpiece. Alternatively the species and the ionizable media may be excited separately (e.g., one excited upstream and another added midstream or downstream, which are then combined prior to delivery to a workpiece).

According to one embodiment of the present disclosure, a plasma system is disclosed. The system includes a plasma device having an active electrode and an ionizable media source configured to supply ionizable media to the plasma device. The ionizable media source is coupled to the plasma device at a first connection upstream of the active electrode. The system also includes a precursor source configured to supply at least one precursor feedstock to the plasma device. The precursor source is coupled to the plasma device at a second connection at the active electrode or upstream thereof. The system further includes a power source coupled to the active electrode and configured to ignite the ionizable media and the precursor feedstock at the plasma device to form a plasma volume.

A method for generating plasma is also contemplated by the present disclosure. The method includes the steps of: supplying ionizable media to a plasma device, supplying at least one precursor feedstock to the plasma device at the active electrode or upstream thereof and igniting the ionizable media and the precursor feedstock at the plasma device to form a plasma effluent.

According to another embodiment of the present disclosure, a plasma system is disclosed. The system includes a plasma device having an active electrode and an ionizable media source configured to supply ionizable media to the plasma device. The ionizable media source is coupled to the plasma device at a first connection upstream of the active electrode. The system also includes a plurality of precursor sources, each of the precursor sources is configured to supply at least one precursor feedstock to the plasma device. Each of the precursor sources is also coupled to the plasma device at a second connection at the active electrode or upstream thereof. The system also includes a power source coupled to the active electrode and configured to ignite the ionizable media and the precursor feedstock at the plasma device to form a plasma volume.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate exemplary embodiments of the disclosure and, together with a general description of the disclosure given above, and the detailed

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description of the embodiments given below, serve to explain the principles of the disclosure, wherein:

FIG. 1A is a schematic diagram of a plasma system according to the present disclosure;

FIG. 1B is a schematic diagram of another embodiment of a plasma system according to the present disclosure;

FIG. 2 is a schematic diagram of a plasma system and a plasma handpiece according to one embodiment of the present disclosure;

FIG. 3 is a flow diagram of an illustrative method according to the present disclosure;

FIG. 4 is a schematic diagram of a plasma system and a plasma handpiece according to one embodiment of the present disclosure;

FIG. 5 is a schematic diagram of a plasma system and a plasma handpiece according to another illustrative embodiment of the present disclosure; and

FIG. 6 is spectra graph of a plasma generated according to one illustrative embodiment of the present disclosure.

DETAILED DESCRIPTION

Plasmas are commonly generated using electrical energy that is delivered as either direct current (DC) electricity or electricity that is alternating current (AC) at frequencies from about 0.1 hertz (Hz) to about 100 gigahertz (GHz), including radio frequency ("RF", from about 0.1 MHz to about 100 MHz) and microwave ("MW", from about 0.1 GHz to about 100 GHz) bands, using appropriate generators, electrodes, and antennas. Choice of excitation frequency determines many properties and requirements of the plasma, the workpiece, as well as the electrical circuit that is used to deliver electrical energy to the circuit. The performance of the plasma chemical generation and delivery system and the design of the electrical excitation circuitry are interrelated—as the choices of operating voltage, frequency and current levels as well as phase all effect the electron temperature and electron density. Furthermore, choices of electrical excitation and plasma device hardware also determine how a given plasma system responds dynamically to the introduction of new ingredients to the host plasma gas or liquid media and the corresponding dynamic adjustment of the electrical drive, such as via dynamic match networks or adjustments to voltage, current, or excitation frequency to maintain controlled power transfer from the electrical circuit to the plasma.

Referring initially to FIG. 1, a plasma system 10 is disclosed. The system 10 includes a plasma device 12 that is coupled to a power source 14, an ionizable media source 16, and a precursor source 18. Power source 14 includes any required components for delivering power or matching impedance to plasma device 12. More particularly, the power source 14 may be any radio frequency generator or other suitable power source capable of producing power to ignite the ionizable media to generate plasma. The precursor source 18 may be a bubbler or a nebulizer, for aerosolizing precursor feedstocks prior to introduction thereof into the device 12. The precursor source 18 may also be a micro droplet or injector system capable of generating predetermined refined droplet volume of the precursor feedstock from about 1 femtoliter to about 1 nanoliter in volume. The precursor source 18 may also include a microfluidic device, a piezoelectric pump, or an ultrasonic vaporizer.

The system 10 provides a flow of plasma through the device 12 to a workpiece "W" (e.g., tissue). Plasma feedstocks, which include ionizable media and precursor feedstocks, are supplied by the ionizable media source 16 and the precursor source 18, respectively, to the plasma device 12.

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During operation, the precursor feedstock and the ionizable media are provided to the plasma device 12 where the plasma feedstocks are ignited to form plasma effluent containing ions, radicals, photons from the specific excited species and metastables that carry internal energy to drive desired chemical reactions in the workpiece "W" or at the surface thereof. The feedstocks may be mixed upstream from the ignition point or midstream thereof (e.g., at the ignition point) of the plasma effluent, as shown in FIG. 1 and described in more detail below.

The ionizable media source 16 provides ionizable feedstock to the plasma device 12. The ionizable media source 16 may include a storage tank and a pump (not explicitly shown) and is coupled to the plasma device 12. The ionizable media may be a liquid or a gas such as argon, helium, neon, krypton, xenon, radon, carbon dioxide, nitrogen, hydrogen, oxygen, etc. and their mixtures, and the like, or a liquid. These and other gases may be initially in a liquid form that is gasified during application.

The precursor source 18 provides precursor feedstock to the plasma device 12. The precursor feedstock may be either in solid, gaseous or liquid form and may be mixed with the ionizable media in any state, such as solid, liquid (e.g., particulates or droplets), gas, and the combination thereof. The precursor source 18 may include a heater, such that if the precursor feedstock is liquid, it may be heated into gaseous state prior to mixing with the ionizable media. In one embodiment, the precursors may be any chemical species capable of forming reactive species such as ions, electrons, excited-state (e.g., metastable) species, molecular fragments (e.g., radicals) and the like, when ignited by electrical energy from the power source 14 or when undergoing collisions with particles (electrons, photons, or other energy-bearing species of limited and selective chemical reactivity) formed from ionizable media 16. More specifically, the precursors may include various reactive functional groups, such as acyl halide, alcohol, aldehyde, alkane, alkene, amide, amine, butyl, carboxylic, cyanate, isocyanate, ester, ether, ethyl, halide, haloalkane, hydroxyl, ketone, methyl, nitrate, nitro, nitrile, nitrite, nitroso, peroxide, hydroperoxide, oxygen, hydrogen, nitrogen, and combination thereof. In embodiments, the chemical precursors may be water, halogenoalkanes, such as dichloromethane, trichloromethane, carbon tetrachloride, difluoromethane, trifluoromethane, carbon tetrafluoride, and the like; peroxides, such as hydrogen peroxide, acetone peroxide, benzoyl peroxide, and the like; alcohols, such as methanol, ethanol, isopropanol, ethylene glycol, propylene glycol, alkalines such as NaOH, KOH, amines, alkyls, alkenes, and the like. Such chemical precursors may be applied in substantially in pure, mixed, or soluble form.

The precursors and their functional groups may be delivered to a surface to react with the surface species (e.g., molecules) of the workpiece "W." In other words, the functional groups may be used to modify or replace existing surface terminations of the workpiece "W." The functional groups react readily with the surface species due to their high reactivity and the reactivity imparted thereto by the plasma. In addition, the functional groups are also reacted within the plasma volume prior to delivering the plasma volume to the workpiece.

Some functional groups generated in the plasma can be reacted in situ to synthesize materials that subsequently form a deposition upon the surface. This deposition may be used for stimulating healing, killing bacteria, increasing hydration (e.g., adding hydroxyl groups to produce carboxyl group at the workpiece), and increasing hydrophilic or hydroscopic properties. In addition, deposition of certain function groups

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may also allow for encapsulation of the surface to achieve predetermined gas/liquid diffusion, e.g., allowing gas permeation but preventing liquid exchange, to bond or stimulate bonding of surfaces, or as a physically protective layer.

With reference to FIG. 2, an illustrative embodiment of the plasma device 12 includes a housing 20 enclosing a dielectric inner tube 22 having a proximal end 25 and a distal end 27 configured for the passage of the plasma effluent in either liquid or gaseous form. The plasma device 12 may be utilized as an electrosurgical pencil for application of plasma to tissue and the power source 14 may be an electrosurgical generator that is adapted to supply the device 12 with electrical power at a frequency from about 0.1 MHz to about 1,000 MHz and in another embodiment from about 1 MHz to about 13.6 MHz.

The precursor source 18 and the ionizable media source 16 are coupled to the plasma device 12 via tubing 13a and 13b, respectively, at a first connection 31. The tubing 13a and 13b may be combined into tubing 13c to deliver a mixture of the ionizable media and the precursor feedstock to the device 12. This allows for the plasma feedstocks, e.g., the precursor feedstock and the ionizable gas, to be delivered to the plasma device 12 simultaneously prior to ignition of the mixture therein.

In another embodiment, the ionizable media source 16 and the precursors source 18 may be coupled to the plasma device 12 via the tubing 13a and 13b at separate connections, e.g., the first connection 31 and a second connection 29, respectively, such that the mixing of the feedstocks occurs within the inner tube 22 upstream from ignition point. In other words, the plasma feedstocks are mixed proximally of the ignition point, which may be any point between the respective sources 16 and 18 and the plasma device 12, prior to ignition of the plasma feedstocks to create the desired mix of the plasma effluent species for each specific surface treatment on the workpiece.

In a further embodiment, the plasma feedstocks may be mixed midstream, e.g., at the ignition point or downstream of the plasma effluent, directly into the plasma. More specifically, the first and second connections 31, 29 may be coupled to the device 12 at the active electrode 23, such that the precursor feedstocks and the ionizable media are ignited concurrently as they are mixed (FIG. 1B). It is also envisioned that the ionizable media may be supplied to the device 12 proximally of the active electrode 23, while the precursor feedstocks are mixed therewith at the ignition point. In other words, the second connection 29 is coupled to the device 12 at the active electrode to achieve mixing that is concurrent with ignition.

In a further illustrative embodiment, the ionizable media may be ignited in an unimixed state and the precursors may be mixed directly into the ignited plasma. Prior to mixing, the plasma feedstocks may be ignited individually. The plasma feedstock is supplied at a predetermined pressure to create a flow of the medium through the device 12, which aids in the reaction of the plasma feedstocks and produces a plasma effluent.

The device 12 also includes an active electrode 23 that extends around or into tube 22. The device 12 may also include an optional return electrode 33 disposed on an outer surface of the tube 22. The electrodes 23 and 33 are capacitively coupled thereto and to the plasma formed within the tube 22. The electrodes 23 and 33 are formed from a conductive material that may be adapted to assist in the ignition of plasma. In particular, the electrode 23 may have a needle or other pointed shape conducive to maximizing local electric field and forming a predetermined ignition point. The electrodes 23 and 33 are coupled to the power source 14, such that

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the energy from the power source 14 may be used to ignite the plasma feedstocks flowing through the inner tube 22. In another embodiment electrode 23 is connected to a separate ignition circuit (not shown) that transfers energy to cause ignition of the plasma species.

In yet another illustrative embodiment, the inner tube 22 may also be formed from a conductive material. In this embodiment, the inner tube 22 is coupled to the power source 14 and igniting electrical energy is transmitted directly through the inner tube 22, or between tube 22 and electrode 23. The inner tube 22 and the electrode 23 may be coupled to the power source 14 through a variety of coupling components, such as wires, cables, antennas and the like. Alternatively, the tube 22 and/or the electrode 23 may be fabricated from conductive materials upon which an insulating layer is formed over at least a portion thereof. In one illustrative embodiment, this may be achieved by forming a metal oxide on a conducting metal or by coating an insulating layer on a conductive material.

The inner tube 22 may be coated by a non-reactive material to reduce plasma species loss through undesired surface reactions. Alternatively, the inner tube 22 may be coated by reactive material that may be removed from the inner tube to create plasma species through tailored plasma driven surface reactions including secondary electron emission or volatilized tube construction material(s). The inner tube 22 may also be coated by an optically reflective material that acts as a means to confine photons generated by the plasma.

The inner tube 22 may have a substantially tubular structure (e.g., cylindrical, granular, etc.). In one embodiment, the distal end 27 may have a high aspect ratio cross-section (e.g., oval, rectangular, etc.). This limits and confines the active plasma volume to provide a flattened plasma effluent. The geometrical confinement of the plasma effluent directs the flow of plasma into open air, imparting a directed hydrodynamic flow of effluent to the workpiece "W" to achieve a highly localized effect on the flow boundary layers. This design provides for enhanced control of the hydrodynamic boundary layers of the plasma effluent and thereby isolates the plasma from the user and minimizes the loss of plasma species (e.g., radicals) to open atmosphere due to an extended length of the boundary layer.

The housing 20 also includes a plasma ignition circuit 24, which includes input controls 26 having one or more buttons or switches 28 for activating the circuit 24. The input controls 26 are coupled to the power source 14 and is adapted to activate the energy flow from the power source 14 to the electrodes 23 and 33. More specifically, the input controls 26 signal the power source 14 to provide a minimum voltage and current suitable for igniting the plasma precursor feedstocks flowing through inner tube 22, such that the plasma precursor feedstocks are ignited and plasma effluent is ejected from the distal end 27 of the inner tube 22. This process can be improved upon by enhancing the "Q" factor of the AC power delivery circuit. The activation circuit 24 may be configured either as a toggle switch or a continuous operation switch. In a toggle mode, the plasma effluent is sustained until the switch is toggled. In a continuous mode, the plasma effluent is sustained for as long as the switch is pressed.

In one embodiment, the activation circuit 24 may also be coupled to the ionizable media source 16 and the precursors source 18 such that upon activation of the activation circuit 24, the power source 14 as well as the flow of plasma feedstocks is also activated simultaneously. Those skilled in the art will appreciate that simultaneous activation may include delaying plasma energy from the power source 14 until the plasma feedstocks reach the inner tube 22; this may be

accomplished by including flow sensors into the tubing 13 and/or the proximal end 25 of the inner tube 22. Alternatively optical sensors may be used to detect the presence or absence of plasma, or with appropriate optical filtering the presence or absence of one or more particular plasma species. A variety of other upstream and downstream mixing and plasma excitation allows tailoring of the relative concentrations of the various plasma species.

FIG. 3 illustrates a method for operating the system 10 according to the present disclosure. In step 100, once the plasma device 12 is brought in proximity with the workpiece "W," the activation circuit 24 is activated to commence the flow of the plasma feedstocks from the precursors source 18 and the ionizable media source 16, respectively. The plasma feedstocks are fed to the plasma device 12, where they are mixed upstream prior to ignition thereof or midstream, e.g., in the ignition region. In step 102, the plasma device 12 signals the power source 14 to supply sufficient energy to ignite the mixed plasma feedstocks. The plasma feedstocks are ignited and plasma effluent is sustained by electrical energy. The ignition induces a variety of physical and chemical reactions in the feedstocks, such as dissociation (e.g., breaking up of molecular components into smaller parts) of the feedstocks into highly reactive species (e.g., radicals, ions, etc.). This plasma environment induces chemical changes to the precursors via a multitude of reactions, including direct electron and photon irradiation directly from the ignited plasma. These chemical changes are contrasted to plasma systems that inject precursors downstream from the active plasma volume in that the present disclosure creates said species in much higher densities and at much higher rates. In step 104, the plasma effluent flows out of the distal end 27 of the inner tube 22 to the workpiece "W." The delivered plasma volume includes various reactive species, such as the functional groups of the precursor feedstock, which are deposited unto the workpiece "W" to react with substituents thereof (e.g., molecules).

FIG. 4 illustrates another illustrative embodiment of a plasma system 110. The system 110 includes a controller 32, which may be a microcontroller, microprocessor or any other suitable logic circuit. The controller 32 may be incorporated into the power source 14. The controller 32 may be coupled to the input controls 26 for controlling the system 110. More specifically, the controller 32 is coupled to the power source 14, ionizable media source 16, and first and second regulator valves 34 and 36. The first regulator valve 34 is coupled to the ionizable media source 16 and controls the flow of the ionizable medium to the plasma device 12. The second regulator valve 36 is coupled to the precursor source 18 and controls the flow of the precursors to the plasma device 12.

As shown in FIG. 4, the device 12 includes an active electrode 43 and a return electrode 45 disposed about an outer surface of tube 22. The electrodes 43 are capacitively coupled to the ionizable media and precursor mix in the tube 22 the extent of their relative positions defining the active plasma volume. The operation of the system 110 may be controlled through the input controls 26. The user may initiate the flow of ionizable media source 16 via the input controls 26. The input signal is then processed by the controller 32, which opens the first and second regulator valves 34 and 36 to open the flow of ionizable media and the precursor feedstock. The first and second regulator valves 34 and 36 may be either opened consecutively or simultaneously. The controller 50 then activates the power source 14 in unison with the flow from the first and second regulator valves 34 and 36 as needed to produce metastable plasma.

FIG. 5 shows another embodiment of a plasma system 120 having multiple precursor sources 40a, 40b and 40c, each

including various types or combinations of precursors. Multiple precursors may be embodied using any of the above-illustrated containers and/or delivery devices. The input controls 26 may include multiple buttons or switches 41a, 41b and 41c for activating each of the precursor sources 40a, 40b and 40c, respectively. In another embodiment, the input controls 26 may be located at any location in the system 120 where manual operation is desired or in the case of automated systems RF power, flow of ionizable media, and chemical precursors may be controlled automatically by the controller 32 based on a feedback algorithm.

EXAMPLES

Argon gas was mixed with CCl_4 and ignited within a plasma activation device. Spectra were obtained for the plasma inside outside device as illustrated by the dashed and solid graphs, respectively in FIG. 6. The graphs illustrate generation of various chemical species as a result of the plasma being produced from an ionizable media and a chemical precursor. The intensity of the various emissions correspond to relative concentrations of different chemical species and they show that as the plasma flows into open air, there is a decrease of the density of some species but an increase in the density in other species. This is due to the plasma mixing with nitrogen, oxygen, carbon dioxide and other constituent gases of air. This exemplar plasma was used to successfully to remove tissue material.

Although the illustrative embodiments of the present disclosure have been described herein with reference to the accompanying drawings, it is to be understood that the disclosure is not limited to those precise embodiments, and that various other changes and modifications may be effected therein by one skilled in the art without departing from the scope or spirit of the disclosure. In particular, as discussed above this allows the tailoring of the relative populations of plasma species to meet needs for the specific process desired on the workpiece surface or in the volume of the reactive plasma.

What is claimed is:

1. An electro surgical system for application of plasma to tissue comprising:
 - an electro surgical pencil including:
 - a housing including a dielectric tube having an optically reflective coating on an inner surface of the dielectric tube; and
 - a removable reactive material coated on the inner surface; and
 - an active electrode;
 - an ionizable media source configured to supply ionizable media to the electro surgical pencil;
 - a precursor source configured to supply at least one precursor feedstock to electro surgical pencil; and
 - a power source coupled to the active electrode and configured to ignite the ionizable media, the removable reactive material, and the precursor feedstock at the electro surgical pencil to form a plasma volume, wherein the at least one precursor feedstock and the ionizable media are mixed and ignited concurrently.
2. The electrosurgical system according to claim 1, further comprising a microcontroller for controlling a flow of the ionizable media and the precursor feedstock.
3. The electrosurgical system according to claim 2, further comprising a first regulator valve coupled to the ionizable media source and a second regulator valve coupled to the precursor source, wherein the first and second regulator valves are coupled to the microcontroller.

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4. The electrosurgical system according to claim 1, wherein the ionizable media is selected from the group consisting of argon, helium, neon, krypton, xenon, radon, nitrogen, hydrogen, oxygen, carbon dioxide, nitrous oxide, and mixtures thereof.

5. The electrosurgical system according to claim 1, wherein the at least one precursor feedstock is a compound having a functional group selected from the group consisting of acyl halide, alcohol, aldehyde, alkane, alkene, amide, amine, butyl, carboxylic, cyanate, isocyanate, ester, ether, ethyl, halide, haloalkane, hydroxyl, ketone, methyl, nitrate, nitro, nitrile, nitrite, nitroso, peroxide, hydroperoxide, oxygen, hydrogen, nitrogen, and combinations thereof.

6. The electrosurgical system according to claim 1, wherein the at least one precursor feedstock is selected from the group consisting of water, haloalkanes, peroxides, alcohols, amines, alkyls, alkenes, alkalines, and combinations thereof.

7. The electrosurgical system according to claim 1, wherein the precursor source includes at least one of a bubbler, a microfluidic device, a nebulizer, a micropump, a piezoelectric pump, or an ultrasonic vaporizer.

8. The electrosurgical system according to claim 1, wherein the electrosurgical pencil includes a return electrode disposed on an outer surface of the dielectric tube.

9. The electrosurgical system according to claim 8, wherein the active and the return electrodes are capacitively coupled to the plasma volume.

10. An electro surgical system for application of plasma to tissue including:

an electro surgical pencil including:

a housing including a dielectric tube having an optically reflective coating on an inner surface of the dielectric tube; and

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a removable reactive material coated on the inner surface; and

an active electrode;

an ionizable media source configured to supply ionizable media to the electro surgical pencil;

a plurality of precursor sources, each of the precursor sources configured to supply at least one precursor feedstock to the electro surgical pencil; and

a power source coupled to the active electrode and configured to ignite the ionizable media, the removable reactive material, and the precursor feedstock at the electro surgical pencil to form a plasma volume, wherein the at least one precursor feedstock and the ionizable media are mixed and ignited concurrently.

11. The electrosurgical system according to claim 10, wherein the electrosurgical pencil includes input controls to activate each of the plurality of the precursor sources individually.

12. The electrosurgical system according to claim 10, further comprising a microcontroller for controlling a flow of the ionizable media and at least one of the precursor feedstock.

13. The electrosurgical system according to claim 1, wherein the electrosurgical pencil is a hand-held electrosurgical pencil, the power source is an electrosurgical generator, and the plasma volume is configured to at least one of substitute or replace surface-terminating species of biological tissue surfaces.

14. The electrosurgical system according to claim 10, wherein the electrosurgical pencil is a hand-held electrosurgical pencil, the power source is an electrosurgical generator, and the plasma volume is configured to at least one of substitute or replace surface-terminating species of biological tissue surfaces.

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